

STUDY OF THE MOLECULAR STRAIN OF POLYMERIZABLE CYCLIC OLIGOCARBONATES USING THE SPECTROSCOPIC TECHNIQUES

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Abstract

Cyclic oligocarbonates, dimer, trimer and tetramer, were synthesized and purified into individual cyclic dimer, trimer and tetramer, respectively. The UV/Vis, IR and Raman spectroscopic techniques were used to study the molecular strain of those cyclics. The UV/Vis data revealed that the λ_{max} due to the phenyl group was shifted from 250 nm for the dimer to 280 nm for the trimer and tetramer. The λ_{max} of the carbonyl group was also shifted from 305 to 316 nm. The extinction coefficient ratio at 254 and 280 nm, $\epsilon_{254}/\epsilon_{280}$, of the dimer was also differed from the others. The results indicated the molecular ring-strained of the dimer. IR and Raman spectroscopic data in the region of 3,700 - 2,400 cm^{-1} , 2,200 - 1,000 cm^{-1} , and 1,000 - 400 cm^{-1} of C-H stretching, carbonate linkage and =C-H bending of the cyclic dimer that were obviously differed from the cyclic trimer and tetramer. The differences were believed to be arisen from the bond angle of the carbonate linkage and the intermolecular interaction of hydrogen on aromatic ring. The torsion angles of the aromatic ring on the isopropylidene group would be suspected as a prime contribution for the molecular strain of these cyclic species.

Keywords: Cyclic oligocarbonates, spectroscopic techniques, molecular strain

Introduction

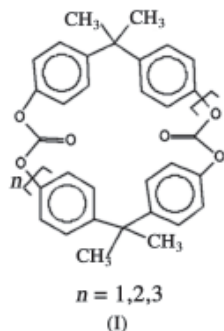
Conventionally, polycarbonates have been manufactured by the interfacial condensation between bisphenol A and phosgene gas. The molecular weight of the polymer is controlled by the stoichiometric ratio between those ingredients. On the other hand, ring-opening polymerization using ionic initiators has given rise to the very high molecular weight polymer (Schnell and Bottenbruch, 1962; Boden *et al.*, 1989; Brunelle *et al.*, 1989; Brunelle *et al.*, 1990). The chain length is also easily controlled. A drawback of this process for the

PCs' production is that the starting cyclic oligocarbonates(I) are difficult to obtain. In 1962, Schnell and co-workers prepared tetrameric cyclic oligocarbonate with a low yield (Schnell and Bottenbruch, 1962). A higher yield was successfully synthesized by *pseudo-high dilution* amine-catalyzed, hydrolysis/condensation reaction of aromatic bischloroformate of bisphenol A (Boden *et al.*, 1989; Brunelle *et al.*, 1989; Brunelle *et al.*, 1990). It had been reported that this reaction mechanism yielded a mixture of cyclic oligomers ranging from dimer

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($n = 2$) to eicosamer ($n = 20$). Other derivatives of oligocarbonates were also achieved (Cella *et al.*, 1989; Guggenheim *et al.*, 1989; Brunelle and Shannon, 1990).



The cyclic oligocarbonates were found to be ring-opening polymerized via the ionic initiators, and the resulting polymers having the molecular weight of more than 20,000 g/mol were achieved (Evans *et al.*, 1989; Brunelle and Shannon, 1990). The molecular weight depended on the monomer and initiator ratio. It was also observed that these cyclic monomers underwent melt polymerization at temperatures above 250°C in the presence of ionic salts (Stewart, 1989). Surprisingly, linear high molecular weight polymers were also obtained under the solid state polymerization without an initiator at the temperature well below their melting temperature (Meekum, 1997).

However, there is no clear evidence in the literature of the mechanism of these polymerization processes. One of the driving forces for the reaction could be the intramolecular ring strain. In this document, spectroscopic techniques will be used to demonstrate the molecular strain of these cyclic compounds.

Methods

All the chemicals used in this study were used as received. The cyclic oligocarbonates were prepared as described by Brunelle *et al.* (1990) and Meekum (1993). The reaction is classified as a *pseudo-high dilution reaction* in which reactants and products in the organic phases are very concentrated and where the reactive intermediates in aqueous phase need to be

diluted to prevent intermolecular reaction. The mixtures of cyclic oligomers were obtained as dried solids.

Each cyclic component was isolated by fractionation techniques that were adapted from the process described by Brunelle *et al.* (1989). Only dimer, trimer and tetramer were obtained in pure crystal solid form.

A UNICAM (Module PU 8735/50) UV/Visible spectrophotometer was employed. The 0.002 M sample solutions were prepared in dioxane and scanned from 260 to 400 nm at a scan rate of 125 nm/min in 10 mm quartz cell. The IR spectra were recorded from a PERKIN ELMER 1720 FTIR at a scan speed of 0.5 cm⁻¹/min using a spectral resolution of 1.0 cm⁻¹ over the wave number range 4,000 - 400 cm⁻¹. The IR samples were prepared by using the KBr disc technique. A BRUKER IFS 60/CS FTIR fitted with a FA 106 FT-Raman module attachment was used to generate the Raman spectra. Solid cyclic samples were lightly pressed into an aluminum funnel sample cup having a 10 mm diameter with a 2 mm diameter tapped hole. Spectra were recorded at the scattered angle of 180° with a spectral resolution of 4.0 cm⁻¹ over 50 to 4,000 cm⁻¹ using a ND/YAG laser at 1,064 nm and power of 100 mW at source. Typically, 100 scans were performed for each analysis.

Results and Discussion

The UV/Vis spectra of each oligomer obtained in the form of solution using 1,4-dioxane as solvent are shown in Figure 1. The spectra indicate two typical absorption spectra having the λ_{max} at 280 and 305 nm for dimer and at 316 nm for the trimer and tetramer, respectively. The first absorption band is due to the electronic transition of phenyl and the later one due to the carbonyl chromophores, respectively. Comparing those spectra, there are an obviously observed shift of the expected absorption band due to the aromatic chromophore from 254 to 280 nm. This shift could be explained by the n to π^* electron interaction of oxygen and the benzene ring. The absorption band due to the n to π^* transition of carbonyl at 316 nm for

trimer and tetramer and 305 nm for the dimer also shifted from below 300 nm. As the results show, it may be explained by the fact that there is a difference due to the nature of oxygen and carbonyl bonding in the carbonate group. When the angle of carbonyl carbon increased due to the bonding strain, the interaction between the n -electron of the ester oxygen and the π -electron of the carbonyl group in the cyclic dimer became stronger. Consequently, the shift of the absorption band to the shorter wavelength of the cyclic dimer is evidenced. The results found also suggested that in the cyclic dimer,

the bond angle of the ester oxygen is larger than it is in the cyclic trimer and tetramer. It is indicated that the dimeric cyclic oligocarbonates are ring-strained in the carbonate linkage.

By measuring the extinction coefficients of the cyclics at 254 nm (ϵ_{254}) and 280 nm (ϵ_{280}), the results in Figure 2(a) show that the extinction coefficients of the cyclics at 254 nm. are linearly increased with the number of aromatic rings in the molecule. However, they are independent of the ring size at the absorption band of 280 nm (Figure 2(b)). The results also illustrate that the $\epsilon_{254}/\epsilon_{280}$ ratios of cyclic trimer and tetramer are almost constant but are obviously different for the dimer (Table 1). This observation strengthens the indication that the dimer molecule is ring-strained.

Table 1. Extinction coefficient of the cyclics at 254 and 280 nm, respectively and the extinction ratio

Compounds	ϵ_{254}	ϵ_{280}	$\epsilon_{254}/\epsilon_{280}$
Benzene	204.0	-	-
Bischloroformate of BPA	763.9	414.4	1.84
Dimer	1,149.0	399.1	2.88
Trimer	1,690.0	134.6	12.66
Tetramer	2,334.0	178.2	13.01

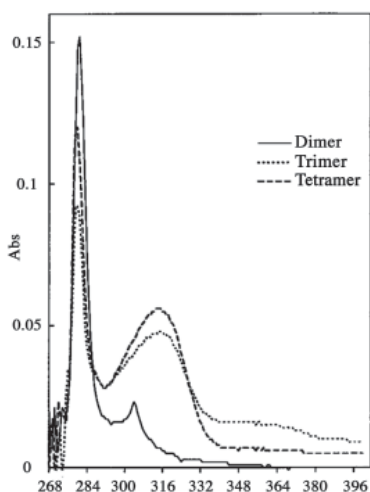


Figure 1. UV/Vis spectra of the cyclic dimer (—), trimer (···) and tetramer (---)

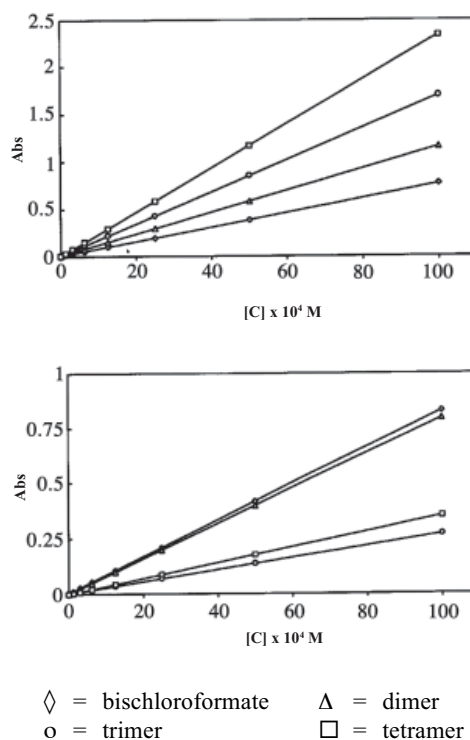


Figure 2. Plots of the absorbance of the cyclics against their concentration at (a) $\lambda_{\max} = 254$ nm and (b) $\lambda_{\max} = 280$ nm

Figure 3 shows the IR spectra of each cyclic component over the 4,000 to 400 cm^{-1} region. There are no major differences in peak characteristics or positions for these three cyclics except for the relative peak intensities of the dimer at 1,000 to 700 cm^{-1} are obvious differences from the others. These will be discussed later on.

From a close observation of the IR spectra of the cyclic in the region 3,700 - 2,400 cm^{-1} correspond to the O-H and C-H of aromatic and aliphatic stretching, there are slight differences in aromatic C-H stretching at 3,200 to 3,000 cm^{-1} for the dimer and trimer. There is a clear split into doublet bands. As the result, it is believed that this could be due to the intermolecular interaction of hydrogen on the aromatic ring of bisphenol A. These findings would be due to the basic hypothesis that the crystal structure of the dimer and trimer is packed more closer than in the tetramer.

The spectra in the region of 2,200 to

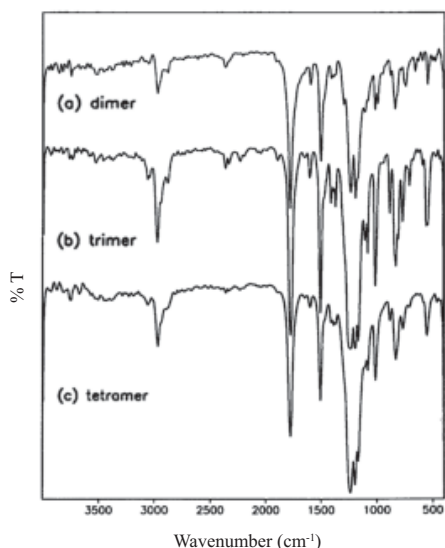


Figure 3. IR spectra of (a) dimer, (b) trimer and (c) tetramer in the 4,000 – 400 cm^{-1} region

1,000 cm^{-1} corresponding to the carbonate linkage and C=C stretching is shown in Figure 4. There is also no significant difference in the IR peak in the area. Upon close observation of C=O stretching at around

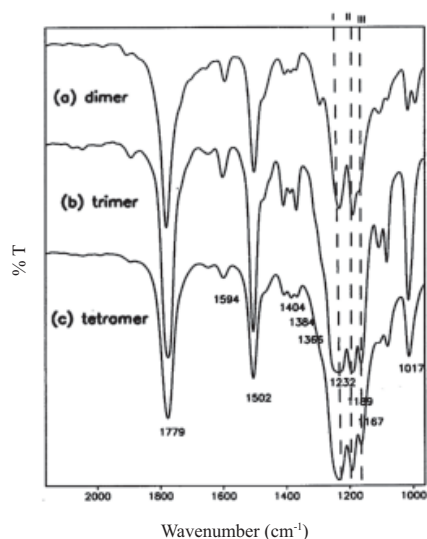


Figure 4. IR spectra of the cyclics in the 2,200–1,000 cm^{-1} region

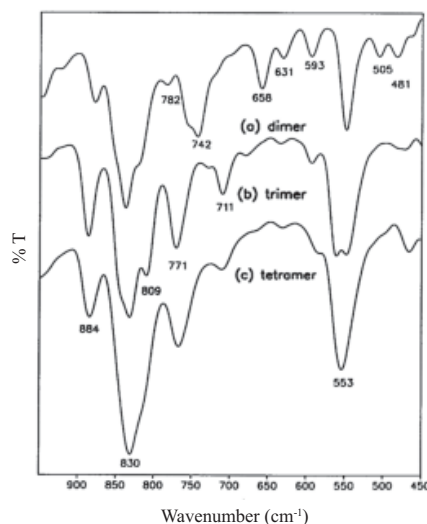


Figure 5. IR spectra of the cyclics in the 1,000 – 450 cm^{-1} region

1,780 cm^{-1} , it is seen that the maximum absorption is shifted to a higher frequency for the dimer than that in the other cyclics. The shift of frequency is believed due to the ring strain of the cyclic dimer. A similar result is also seen in

the IR spectra in the region of 1,000 to 400 cm^{-1} which is $=\text{C-H}$ bending at 884 to 821 cm^{-1} , as illustrated in Figure 5. The vibration band of the bending is split into four peaks. It is noticed that the resolution of the peaks becomes less resolved as the ring size becomes bigger. It is also caused by the ring strain.

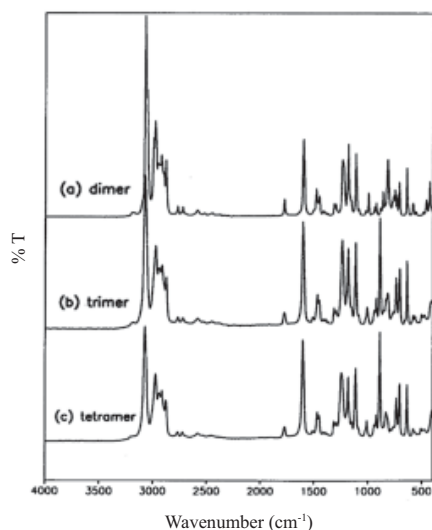


Figure 6. Raman spectra of the cyclics in the 4,000 – 400 cm^{-1} region

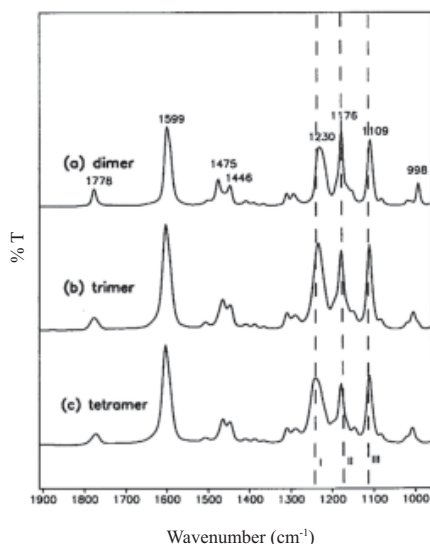


Figure 7. Raman spectra of the cyclics in the region 2,000 – 1,000 cm^{-1} region

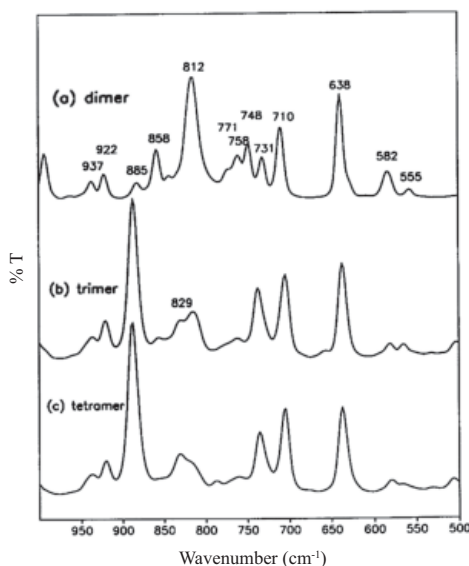


Figure 8. Raman spectra of the cyclics in the 1,000 – 500 cm^{-1} region

the peak intensity of the vibration between the dimer and the others. The former has its strongest peak intensity at 812 cm^{-1} but the others show at 887 cm^{-1} . The bending peak of the dimer also has five intense and well resolved bands but there are only two intense peaks for the other cyclics. The likely explanation for these observations is due to the intermolecular interaction of C-H aromatic bending and the angular strain of carbonate linkage, respectively. These phenomenon would cause a change in the vibrational symmetry properties of those species resulting in the change in the intensity of the Raman effect.

The results of the UV, IR and Raman spectroscopic data reveal that there are many similarities in the spectroscopic nature of the cyclic components especially between the trimer and tetramer. However, the dimer can be distinguished from the rest but with great difficulty. The differences arise typically from the bond angle of the carbonate linkage and the intermolecular interaction of the aromatic hydrogen.

Conclusion

It was proposed that ring strain in cyclic oligocarbonates is the main driving force for the polymerization of these cyclic monomers. The UV/Vis data revealed that the λ_{max} due to the phenyl group was shifted from 250 nm for the dimer to 280 nm for the trimer and tetramer. The λ_{max} of the carbonyl group was also shifted from 305 to 316 nm. The extinction coefficient ratio at 254 and 280 nm, $\epsilon_{254}/\epsilon_{280}$, of the dimer was also differed from the others. The results indicated the molecular ring-strained of the dimer. IR and Raman spectroscopic data in the region of $3,700 - 2,400\text{ cm}^{-1}$, $2,200 - 1,000\text{ cm}^{-1}$ and $1,000 - 400\text{ cm}^{-1}$ of C-H stretching, carbonate linkage and $=\text{C-H}$ bending of the cyclic dimer that were obviously differed from the cyclic trimer and tetramer. The differences were believed to be arisen from the bond angle of the carbonate linkage and the intermolecular interaction of hydrogen on aromatic ring. The torsion angles of the aromatic ring on the isopropylidene group

would be suspected as a prime contribution for the molecular strain of these cyclic species.

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